IPST Technical Paper Series Number 609

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March 1996

Submitted to
Environmental Science & Technology

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Abstract

Batch sorption experiments for the retention of 2,4-dichlorophenol and 2,4,5-trichlorophenol by pulped wood fibers indicate that sorption is governed by the interaction of the acid form of these compounds with lignin. Measurements of fiber-water distribution coefficients over a pH range of 2 to 12 demonstrate that chlorophenolate ions do not sorb to the solid phase, and the interaction between the neutral form of the compound and lignin is primarily responsible for the retention within this pH region. This was confirmed by experiments using lignin and cellulose model particles and pulp fibers of various lignin content. The results have led to the development of an equation that relates the overall fiber-water distribution coefficient to the ionization of the phenol, the lignin mass fraction of the fiber, and a lignin-water distribution coefficient which can be estimated with a linear free-energy relationship.

Modeling the fiber-water transfer of chlorophenols based on the dominance of the hydrophobic interactions was successful in the treatment of concentration, temperature, and inorganic salt effects. Sorption isotherms were shown to be linear and to have no dependency on phenol cosolutes at concentration levels common in bleaching. Distribution coefficients demonstrated only a slight dependency on temperature and inorganic salt concentrations which could be predicted from the solute's heat of aqueous dissolution and Setschenow constants, respectively. Measurements also indicate that sorption is unaffected by fiber surface area and concentration, but do show dependency on the concentration of colloidal materials which appear to be the result of third-phase sorption.

Introduction

Bleaching of pulped wood fibers generates a wide array of chloro-organic compounds varying in molecular weight and functionality (*1-5*). The fiber-water distribution of these chemicals is a major factor governing their transport through the treatment system and into the environment. This study establishes the sorption fundamentals of two model compounds, 2,4-dichlorophenol (2,4-DCP) and 2,4,5-trichlorophenol (2,4,5-TCP), to pulp fiber and its components. These compounds are significant in their own right in that they are formed during bleaching (*6,7*), but more importantly, possess a blend of hydrophobic and ionizable groups typical of those found in many other bleaching residuals (*8-10*). Thus, understanding the role of fiber components and the effect of variables such as ionization, cosolute interactions, inorganic salts, and temperature on the sorption of these chemicals will provide insight on the transport of several species found in bleaching effluents.

A processed wood fiber is a composite structure composed mainly of cellulose and lignin. The chemical differences between these components result in significant variability in their ability to interact with water; the polyhydroxyl structure of cellulose provides for strong hydrogen bonding, while lignin's phenylpropane units produce relatively hydrophobic regions. There is evidence (*11-15*) that these variations in sorbent hydrophilicity strongly impact its retention of organic chemicals; significant reductions and even the elimination of sorption occurs with increasing sorbent oxidation levels. Comparisons with cellulose and lignin model particles as sorbents demonstrate that aqueous toluene and trichloroethylene have a much higher affinity for lignin (*16*). This indicates that lignin may dominate the sorption of nonpolar organic species to pulp fibers and fiber solids much in the same way that organic matter

dominates sorption in soils and sediments (*17-20*). But chlorophenols are not completely nonpolar species. The presence of an ionizable hydroxyl group creates the potential for both hydrogen bonding and interactions between the compound's ionized form and the fiber surfaces. The impact of the hydroxyl group is difficult to gauge for the neutral form of chlorophenol compounds. It is generally noted that hydrogen bonding can dramatically increase sorption (*21-23*), but studies on the aqueous sorption of phenols to various organic sorbents conflict on this issue (*24-26*). The fact that some studies report an increase of sorption with greater sorbent oxidation levels while others report either no effect or a decrease may indicate that sorption enhancement due to the creation of specific bonding sites may be offset by the sorbent's increased hydrophilicity.

For ionized chlorophenols, the effect of the charged functional group on sorption is expected to be significant. Ionized organic compounds are much more water soluble than their conjugate acids. Measurements of organic-phase/water distributions for various organic acids indicate that the neutral form dominates partitioning if pH is less than 2 units above the solute's pK_a value (*27-29*). But in situations where the ionic form of the chlorophenol is strongly dominant in solution, some studies have indicated that the sorption of the organic ion cannot be neglected; chlorophenol sorption to soils and sediments remains strong even after the compound is completely ionized (*29-31*).

Previous studies of chlorophenol sorption to organic sorbents under alkaline condition also indicate that the participation of the phenol's ionized form is greatly enhanced by the presence of inorganic ions. It is thought that the chlorophenolates can ion-pair with inorganic cations to form hydrophobic species which dominate the sorption process. The evidence for

this mechanism comes from studies of the octanol-water distribution of chlorophenols which indicate the strong presence of ion-paired chlorophenolates in the octanol phase (*27,28*), and from increases in the solid-water distribution of chlorophenols at high pH levels due to increased ionic strengths (*29,31*). Although these results do point to the participation of inorganic ions in the distribution of the ionized chlorophenols, other mechanisms are possible. At relatively high inorganic salt concentrations, the "salting out" of organic solutes can strongly increase their solid-water distribution.

Other variables that might affect the sorption of chlorophenols to pulp fibers are the presence of cosolutes and colloidal material. Bleaching filtrates in a kraft paper mill contain a rich variety of organic chemicals, but the concentration of any one chemical is low. Thus, each of numerous cosolutes present in the aqueous phase of the effluents can be considered to be infinitely dilute. Given their low concentration, cosolute effects are expected to be minimal, but it is possible they will impact the process as cosorbates. This effect is difficult to predict without a mechanistic model of the sorption process, but it does appear that, in some cases, low levels of cosolutes acting as cosorbates can significantly drop the distribution of a nonpolar organic (*32*). Possible "third-phase" effects are also of concern in bleaching effluents because of the high concentration of colloidal or macromolecular material. This material may offer organic solutes a region into which they can partition to escape the aqueous phase (*33-38*). There is evidence for this third-phase partitioning in other systems (*13,39-43*). The mechanism appears to be similar to that for larger sorbents. Just as the polarity of a solid substrate and the aqueous activity coefficient of a solute are shown to affect solid-water distributions,

experiments that measure the retention of organic solutes by colloidal materials indicate that sorption is dependent on both colloid and solute hydrophobicity (*44-46*).

Theory

The distribution coefficient is defined as the ratio between the solute concentration retained by the solid or fiber phase, C_s, and the solute concentration remaining in the aqueous solution, C_w. Pulped wood fibers separated from an aqueous solution retains a significant volume of water (*47-50*). Thus, C_s can be divided into three independent contributions which include the mass of solute retained by cellulose, s_c, lignin, s_l, and the solute which is retained in the water of the solids, s_w, divided by the oven dried mass of fiber, $m_{o.d.}$

$$C_s = \frac{s_c + s_l + s_w}{m_{o.d.}} \tag{1}$$

Equation 1 can be rewritten in terms of the oven-dried mass fractions and solute concentrations in cellulose and lignin, f_c, f_l and C_c, C_l, respectively

$$C_s = f_c C_c + f_l C_l + \frac{s_w}{m_{o.d.}} \tag{2}$$

By dividing through by the concentration of the solute in the aqueous phase, C_w, the fiber-water distribution coefficient can be expressed in terms of sorption contributions from the cellulose-water, K_c, and lignin-water, K_l, distribution coefficients as

$$K_d = f_c K_c + f_l K_l + \frac{s_w}{C_w m_{o.d.}} \tag{3}$$

Assuming the water held by the fiber phase is similar to the aqueous solution from which it was separated, the mass of solute in the fiber water can be expressed in terms of the volume of water retained, V_{fw}, and the concentration of the solute in the aqueous solution, C_w

$$s_w = V_{fw} C_w \tag{4}$$

Since the consistency of the fiber phase, C_f, is defined as

$$C_f = \frac{m_{o.d.}}{\text{mass wet fiber}} \tag{5}$$

V_{fw} can be written in terms of C_f as

$$V_{fw} = \frac{1}{\rho}\left(\frac{1}{C_f} m_{o.d.} - m_{o.d.}\right) \tag{6}$$

where ρ is the density of the aqueous solution. Substituting eqs. 4 and 6 into eq. 3 yields

$$K_d = f_c K_c + f_l K_l + \frac{1}{\rho}\left(\frac{1-C_f}{C_f}\right) \tag{7}$$

The last term in this equation can be thought of as the water retention coefficient, k_w, defined as

$$k_w = \frac{1}{\rho}\left(\frac{1-C_f}{C_f}\right) \tag{8}$$

The mass fraction of lignin in a pulp fiber, f_l, is typically reported within the paper industry by a kappa number, η. By definition, kappa number is the volume of 0.1N potassium permanganate solution consumed by one gram of moisture-free pulp under the conditions specified by the test method (*51*). The permanganate oxidizes the non-cellulosic or lignin portion of the pulp fibers. The kappa number is related to the lignin mass fraction through the equation (*51*),

$$f_l = 0.0015\eta \tag{9}$$

The substitution of eq. 9 as well as 1 - f_l for f_c into eq. 7 results in a linear relation between kappa number and measured fiber-water distribution coefficients for aqueous organic compounds

$$K_d = \frac{1}{\rho}\left(\frac{1-C_f}{C_f}\right) + K_c + 0.0015(K_l - K_c)\eta \tag{10}$$

As discussed earlier, sorption of chlorophenolates to natural organic matter is small in comparison to the sorption of their neutral form. This allows it to be neglected in situations where only a small fraction of a compound is ionized. Under these conditions, sorption can be estimated as the fraction of the compound in the neutral form, α, multiplied by the neutral compound's distribution coefficient, K_d^0,

$$K_d = k_w + \alpha K_d^0 \tag{11}$$

where α is calculated using the compound's pK_a and the pH of the aqueous phase

$$\alpha = \frac{1}{1+10^{(pH-pK_a)}} \tag{12}$$

Substitution of eq. 11 into eq. 10 gives

$$K_d = \frac{1}{\rho}\left(\frac{1-C_f}{C_f}\right) + \alpha\left[K_c^0 + 0.0015(K_l^0 - K_c^0)\eta\right] \tag{13}$$

where K_c^0 and K_l^0 represent the cellulose-water and lignin-water distribution of the neutral form of the solute.

Materials and Methods

Materials. Softwood pulp fibers and cotton linters (100% cellulose fibers) were obtained from Georgia-Pacific Corporation. The pulp was thoroughly washed to remove residual processing chemicals, and the average kappa number (lignin content) of each sample was determined (51). The fiber containing lignin was all brown stock from a kraft pulping process with the exception of the kappa number 4.93 that was collected from the second stage of a ClO_2 based bleaching sequence. The fibers were centrifuged to 30% consistency (solids content) and stored at 5°C. The consistency of the samples was never allowed to rise above 35% to preserve the pore structure of the fibers. Model lignin material, precipitated from the effluents of softwood kraft pulping operations and sold commercially as Indulin AT, was obtained from the Westvaco Chemical Division (Charleston Heights, SC) in a dried, powder form. The chemicals, 2,4-DCP and 2,4,5-TCP (> 98% purity levels), were purchased from Chemservices (West Chester, PA). Radiolabeled chlorophenols were purchased from Sigma Chemical Company (St. Louis, MO). Both [^{14}C] 2,4-DCP (8.42 mCi/mmol) and [^{14}C] 2,4,5-TCP (4.40 mCi/mmol) were stored in amber vials as methanol solutions at 2°C. 2,4-DCP was > 98% pure and 2,4,5-TCP was > 99% pure as determined by HPLC. Scintillation counting was done on a Beckman (Fullerton, CA) Model LS 3801 Scintillation Counter. Scintiverse E Scintillation Cocktail (Fisher, Pittsburgh, PA) was used for all solution phase samples, and Sigma-Fluor™ Universal LSC Cocktail was used with the fiber samples.

Determination of Acid Dissociation Constants. Since pK_as reported for 2,4-DCP and 2,4,5-TCP strongly depended on the conditions under which they were measured, it was necessary to

measure these values under the pH, temperature and low ionic strength conditions used in the sorption studies. The conjugate bases of both the di- and trichlorophenol had significantly different absorption spectra from those of their acid forms, which allowed their pK_as to be determined spectrophotometrically (*52*). Spectra were taken on a Perkin-Elmer (Norwalk, CT) Lambda 4B UV/VIS instrument. At 25°C, $pK_a = 7.87 \pm 0.05$ for 2,4-DCP and $pK_a = 6.92 \pm 0.02$ for 2,4,5-TCP in distilled water adjusted for pH with weak HCl and NaOH solutions.

Bulk Solution Retention by Fibers. Consistency values, C_f, for estimating k_w in eq. 8 were determined by combining 20 mL of an aqueous buffer and 50 mg of fiber in 20 mL vials. The sample was thoroughly mixed and allowed to stand for three days. The fibers were filtered as described below. Consistency was then determined by transferring the wet fibers to a heated balance (110°C) and measuring their initial and final (oven-dried) mass. The k_w term thus determined varied from 2 to 6 mL/g with an average value of 4 mL/g.

Grinding Pulp Fibers. The effect of fiber surface area was tested by measuring the sorption of model compounds to kappa number 69.8 fibers which had been dried and ground into powder using a Wiley Mill. Image analysis on the fibers showed that most of the ground fiber particles (> 80%) had lengths of less than 0.1 mm and could be categorized as fines, while none of the unground fibers fell into this category. The arithmetic average fiber length for the ground fibers (0.09 mm) was more than an order of magnitude lower than that for the unground fibers (1.90 mm). These results indicate that grinding dramatically changed the structure of the fibrous solids which likely resulted in a substantial increase in fiber surface area.

Image analysis data were extracted with a Zeis (Hanover, MD) Axioskop microscope equipped with a CDC (Boyertown, PA) Model I RGB camera, and a Vision Plus-AT image driver board (Imaging Technology, Bedford, MA). The data were processed with the Optimas (Bioscan, Edmonds, WA) 4.0 Image Analysis Program.

Generation of Colloidal Phase. Lignin colloid or third-phase solutions were produced by leaching lignin precipitate samples (Indulin AT) with distilled water. This was done using a pressurized filtration stir cell (Amicon, Beverly, MA) in which the solid phase was retained by a 0.05 μm, polycarbonate filter (Poretics, Livermore, CA). The levels of organic carbon (TOC) present in the aqueous filtrate were determined using a Shizmadzu (Kyoto, Japan) Model TOC-5050 Total Organic Carbon Analyzer. It was found that the level of third-phase material in a pulp slurry correlated with the absorption of light at a wavelength 276 nm determined on a Perkin-Elmer (Norwalk, CT) Model Lambda 4B UV/VIS Spectrophotometer. For studies in which the level of colloidal materials was raised in sorption samples, dilutions of an initial concentrated colloid solution were used as the aqueous phase. The TOC levels in samples could be calculated from the initial level in the stock solution and checked through light absorption.

Sorption Experiments. Twenty mL of distilled water or a weak aqueous buffer were combined with 50 mg (oven-dried) of fibers in amber vials with Teflon lined caps. In samples where a buffer was not used, pH was adjusted with small amounts of weak HCl and NaOH solutions (for all samples not included in KCl studies, ionic strength was maintained at < 0.005

M). Through a methanol carrier, either 2,4-DCP (108 nCi) or 2,4,5-TCP (46.7 nCi) was added to produce a 100 ppb solution (with methanol levels of < 0.01% by volume). In cases where higher sorbate concentrations or other sorbates were needed (e.g., in isotherm studies), unlabeled chemicals were added to the base (labeled) sorbate. For solids effect measurements, 50 mg (oven dried) of pulp was again used and the concentration of the aqueous phase was varied. The components of the samples were thoroughly mixed and allowed to equilibrate. Time course measurements showed 4 days was more than sufficient for equilibration. The pH was then determined and the fibers were vacuum filtered using 0.1 μm Anopore™ Inorganic Membranes (Alltech, Deerfield, IL) and placed into a 20 mL scintillation vial. Triplicate measurements were made of the separated aqueous solution phase which were quench-corrected with chemical quench curves generated using ^{14}C standards purchased from Beckman.

Chlorophenols associated with the fiber were leached out by adding 4.32 mL of water and methanol, 180 μL of acetic acid (to reduce chemiluminesence), and an aqueous scintillation cocktail (12 mL) to the fibers in a scintillation vial. The mixture was agitated and allowed to settle over 4 days. The vial was then counted and the counts quench corrected using standards containing varying amounts of fiber. Overall mass balances were between 98.4 and 100%.

It was very difficult to obtain an accurate dry weight of the fibers taken for counting. Water constitutes a substantial (≈65%) and variable part of the fiber mass, and it was, therefore, necessary to directly measure the weight of the fibers counted. Fortunately, the degree of quench was sensitive to the fiber mass added. Standard plots of the quench factor (H number) vs. the amount of dry fiber added were very linear (typically, $r^2 \geq 0.97$), and the

weight of the fiber transferred for counting in the sorption experiments could be directly obtained from the amount of quenching (*53*). Measured distribution coefficients typically had standard deviations of better than ±3 mL/g.

Sorption to model lignin precipitates could be determined from concentration changes in the solution phase. For these samples, a solution of either 2,4-DCP (108 nCi) or 2,4,5-TCP (46.7 nCi) was mixed and triplicate measures of the solution phase concentration were taken. The solution was then added to amber vials with Teflon lined caps (20 mL), 100 mg of the precipitate was added and the samples were mixed for 4 days. The solids were separated from the solution phase using vacuum filtration (as described earlier) and the solution concentration was tested again. The difference in concentration and the precipitate mass could then be used to calculate a K_d value. The solid phase was dissolved in ethylene glycol and a portion of this solution was used to determine recoveries. Mass balances of > 98% were achieved.

Results and Discussion

Isotherms. Figure 1 illustrates the isotherm for the sorption of 2,4,5-TCP to kappa number 69.8 softwood fibers. Here, the chlorophenol concentration was varied from less than 1 ppb to more than 1 ppm. The isotherm is clearly linear, i.e., K_d is independent of chlorophenol concentration. This result and similar results for the sorption of both 2,4-DCP and 2,4,5-TCP to various lignin level pulps ($r^2 \geq 0.99$) indicate a linear model of sorption can be used quite accurately in the concentration regime appropriate to bleaching effluents.

To determine if surface area plays a role in the sorption process, pulp fibers were mechanically ground into powder and used as sorbents in distribution measurements. Table 1

shows a comparison of the solid-water distribution coefficients for the sorption of model compounds to both the ground and unground pulp fibers. The results demonstrate that the increased surface area had no effect on sorption. Experiments were also run to determine if the presence of other chlorophenols would change the shape of the measured isotherms (e.g., through competitive sorption). Figure 2 plots the isotherm of 2,4,5-TCP for the sorption to kappa number 69.8 softwood fibers using a series of chlorophenols as cosolutes including a five chlorophenol mixture (2-chlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,5-tetrachlorophenol, and pentachlorophenol). These results and similar results for 2,4-dichlorophenol again show no effect.

pH Dependency and Chlorophenolate Sorption. Figure 3 shows the distribution of 2,4,5-TCP between distilled water and kappa number 105 softwood pulp fibers as a function of pH. The solid curve represents the sorption predicted for the compound by eqs. 11 and 12 using the measured k_w value of 4 mL/g and the measured distribution coefficient below a pH of 4 as the neutral compound distribution coefficient, K_d^0. The good fit indicates that the ionized form of 2,4,5-TCP does not sorb to the pulp fibers, at least not under the low ionic strength conditions used. Figure 4, which plots the sorption of both 2,4-DCP and 2,4,5-TCP to a kappa number 69.8 softwood pulp as a function of pH, further confirms these results and also shows an interesting situation in which the sorption of the trichlorophenol, which typically has the higher sorption, drops below that for the dichlorophenol in the pH range of about 7.7 to 9. For a bleached kraft paper mill, the primary clarifier influent will typically have a pH of greater than

7. From this figure, it is apparent that any prediction of a chlorophenol's distribution in bleaching effluents must take into account the effects of ionization on sorption.

Figure 5 shows the fit for the sorption of both the di- and trichlorophenol to a kappa number 69.8 softwood fiber. Here, the measured distribution coefficients were plotted as a function of α (eq. 12) which, according to eq. 11, should produce linear fits with the slopes providing estimates of the neutral compound's solid-water distribution coefficient, K_d^0. Data were collected in the pH range of 6-10 to represent the typically alkaline conditions found in kraft mill primary clarifiers. Slopes for 2,4-DCP and 2,4,5-TCP are 119 and 42.0 mL/g, respectively, match the K_ds measured below a pH of 4 in Figure 4 where the chlorophenols are entirely in their neutral form. These results conflict with the work of others on the role of ionized phenols in the sorption to soil and sediment samples (*27-29*). As was noted earlier, it has been argued that while neutral chlorophenols dominate sorption, sorption of the ionized form cannot be ignored at high pH. This may be due to the sorption of the conjugate base to the mineral fraction of the soil and sediment samples, or the fact that most of the data in these studies included highly chlorinated phenols which remain relatively hydrophobic even after ionization. But for the sorption of the di- and trichlorinated phenols to pulp fibers, it is clear that the ionized form plays no role in sorption at pH 2-12, indicating the only mechanism of concern is the water-solid distribution of the neutral compound.

The Lignin-Water Distribution Coefficient. Figure 5 is an example of the data collected for both model compounds over a full range of lignin content pulps starting with cotton linters (100% cellulose fibers) and ending with kappa number 105 softwood fibers. By plotting the

data in this fashion, a comparison of the sorption for the di- and trichlorophenol compounds can be made at the same level of ionization. This provides for a more direct comparison of the affinity of these compounds for the pulp fibers. In every case there is a significantly higher sorption for trichlorophenol over dichlorophenol. The data also demonstrate the importance of lignin in the retention process. As shown in Table 2, a steady increase in K_d (for the neutral compound) is found with increasing lignin, and sorption to the lignin precipitates is more than two orders of magnitude greater than sorption to the cotton linters (cellulose) for both compounds. This indicates that the cellulose-water distribution coefficient, K_c^0, in eq. 13 can be neglected to give eq. 14

$$K_d = \alpha f_l K_l^0 \tag{14}$$

Here, k_w is neglected and f_l replaces the estimate of lignin mass fraction based on the fibers' kappa number. In Figures 6 and 7, plots of fiber-water distribution coefficients versus kappa number (related to lignin mass fraction through eq. 9) at two different pH levels are given for both 2,4-DCP and 2,4,5-TCP. The plots again demonstrate the inversion of sorption between the di- and trichlorophenol under alkaline conditions due to the differences in their pK_a values. The linearity of these plots also allows estimates of K_l^0 values to be made from the slopes. The estimated values from the average of the three slopes using eq. 13 are 360 mL/g and 1200 mL/g for 2,4-DCP and 2,4,5-TCP, respectively, which are consistent with the measured K_l^0 values for the model lignin material (Table 2).

The results indicate eq. 14 provides a good approximation of fiber-water distribution for chlorophenols and by extension to organic compounds based on measures of fiber lignin, solute pK_a, pH of the aqueous solution, and the lignin-water distribution coefficient. K_l^0 can be

estimated from a linear free-energy relationship. Figure 8 plots log K_l^0 of four compounds versus the log of their octanol-water distribution coefficients, log K_{ow}. Values for trichloroethylene and toluene were taken from a study based on the same lignin material used here (*16*). Although the plot combines two sets of data collected under different experimental protocols, it is still strongly linear. The resulting equation

$$\log K_l^0 = 0.95 \log K_{ow} - 0.48 \tag{15}$$

provides a first estimate for the neutral fraction lignin distribution coefficient for organic chemicals.

Temperature and Inorganic Salt. With the fiber-water distribution coefficient for chlorophenols being dominated by the lignin-water distribution coefficient of the neutral form of the compound and the linear isotherms over the concentration region of interest, the fiber-water system tends to be quite similar to the soils or sediments-water systems. Extending this analogy, the sorption process can be treated as the phase distribution with lignin as an accommodating phase to the chlorophenols, which would be expected based on similarities in their structures. The effect of temperature and inorganic salts can then be predicted based on their effect on the chlorophenols aqueous activity coefficients. The results are equations 16 and 17 for predicting the functional relationship between sorption and temperature and inorganic salt, respectively (*54*).

$$\ln K_d = \frac{-\Delta H_{sorp}}{RT} + \text{Constant} \tag{16}$$

$$\log K_d = \log K_d^0 + K^s[\text{salt}] \tag{17}$$

Here, ΔH_{sorp} is the heat of sorption, R is the gas law constant, and T is absolute temperature in eq. 16, and K_d^0 is the distribution coefficient with no salt present, K^s is the Setschenow constant for the solutes, and the inorganic salt levels are measured in molarity in eq. 17.

Figure 9 plots ln K_d against 1/T in accordance with eq. 16. The data cover the temperature region of environmental interest and appear to show strong linear correlations. The estimates for the heats of sorption from the slopes of these lines are -1.8 and -2.6 Kcal/mol for 2,4-DCP and 2,4,5-TCP, respectively. Given the heats of aqueous dissolution at 25°C (55-58) for benzene (0.50 Kcal/mol), phenol (1.7 Kcal/mol), and pentachlorophenol (3.92 Kcal/mol), these values appear to be consistent with the enthalpy associated with aqueous dissolution. Thus, temperature effects should be predictable from solubility information, but the results also indicate that K_d has only a weak temperature dependency. For a 20°C increase which might be associated, for example, with a seasonal change, the distribution coefficient would drop by only 16%. This small temperature dependency may be augmented or offset by the temperature dependency of an organic acid's pK_a value. A chlorophenol's pK_a may decrease or increase with temperature; the extent of which is dependent on the specific phenol, but shifts are usually in the range of 0.01 to 0.03 pK_a units per degree rise in absolute temperature (*52*). Thus, for organic acids, estimates of temperature effects must also take into account the temperature dependency of pK_a.

Figure 10 plots K_d as a function of pH for the sorption of 2,4,5-TCP to kappa number 69.8 softwood fibers at two different inorganic salt levels. The plot demonstrates the importance of the salting out mechanism with the use of potassium chloride. At the lower pH values where the trichlorophenol will be completely in its neutral form, the presence of salt

causes a strong increase in the sorption. At high pH levels where the trichlorophenol is completely ionized, sorption is eliminated under both high- and low-salting conditions. These results are consistent with a salting out mechanism, while the lack of sorption at high pH levels is inconsistent with ion pairing. Further evidence for the salting out mechanism comes from plots of K_d vs. the fraction of the compound in its neutral form. From previous measurements on this system, it was found that sorption is isolated to the neutral form of the chlorophenol compounds. As demonstrated in Figure 11, the sorption of 2,4-DCP at both low ionic strength and at high KCl concentrations starts out at the same point when the compound is completely in its ionized form (i.e., no sorption). But as the population of the neutral molecules increases, the two lines diverge with the sorption under high inorganic salt concentrations having the higher slope. This indicates that the salting out of neutral compounds, rather than the participation of the chlorophenolate species, causes the increased sorption.

Plots of log K_d for the sorption of 2,4-DCP and 2,4,5-TCP by kappa number 105 softwood fibers against the molar concentration of KCl are linear ($r^2 \geq 0.90$), as expected on the basis of the salting out mechanism (eq. 17). The slopes of these lines are 0.14 and 0.22 $L \cdot mol^{-1}$ for di- and trichlorophenol, respectively. These estimates are consistent with salting constants for other salts and organic solutes which range from about 0.1 to 0.4 $L \cdot mol^{-1}$ (59-62). For the distribution of chlorophenols in bleaching effluents, these results indicate that the effect of inorganic salts will be small. For most paper mills, the concentration of ions in effluent streams typically will be low (< 100 ppm). At these levels, the predicted salting effects will be negligible. But as the industry moves towards greater mill closure (process water recycling), these concentrations as well as the salting effect phenomenon are expected to climb. It should

be noted that KCl was the only salt tested here. The choice of KCl was somewhat arbitrary, but consideration was given to the fact that past sorption studies had attributed increased sorption of chlorophenol chemicals by sediments to an ion-pairing mechanism with potassium (using a KCl solution).

Solids Concentration and Colloidal Material. Results from a study testing the effect of fiber concentrations on the sorption 2,4,5-TCP to kappa number 69.8 softwood fibers are listed in Table 3. The results show no measurable solids effect (*33-35,63-65*). Although no solids concentration effect was apparent in laboratory experiments, the large amount of color that exists in the bleaching effluents raises the issue of how excessive colloidal materials will impact the distribution process. Total Organic Carbon (TOC) levels measured in the filtrates of fiber sorption experiments indicate that colloidal levels are low (< 5 ppm TOC), but the results also indicate that these levels climb linearly with solids concentration, and increases strongly with the kappa number of the fibers. For effluents from a pulp and paper mill, levels of the colloidal materials, much of which is lignin-derived, may be almost two orders of magnitude greater than that found in laboratory experiments. To determine the effect of these high levels, lignin precipitate materials were leached under high pressures to produce TOC levels in excess of 200 ppm. Dilutions of this third-phase solution were then used in sorption experiments.

The results indicate that the presence of the derived colloidal phase which ends-up in the filtrate does drop sorption, but it requires a significant amount of material to do this. Rough estimates from this data indicate that the colloid-water distribution coefficients are of the same order of magnitude as the lignin-water distribution coefficients. Considering that the

surface area of the colloidal material is probably several orders of magnitude greater than that of the solid lignin material, the results are more consistent with a mass-based sorption process as found by previous studies (46). The mechanism and magnitude of this retention is important because the colloidal material in bleaching effluents will not be settled out at the primary clarifier, therefore, these materials can effect the survival of organic materials during secondary treatment, as well as their transport once released into the environment.

Acknowledgments

We thank the Member Companies of the Institute of Paper Science and Technology for supporting this research, and Tom Kemeny of the Georgia-Pacific Corporation for several discussions. Portions of this work were used by S.J.S. as partial fulfillment of the requirements for the Ph.D. degree at IPST.

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Table 1. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to ground and unground, kappa number 69.8 softwood fibers at a pH of 7.00.

	unground K_d(mL/g)	ground K_d(mL/g)
2,4-dichlorophenol	46.4	46.2
2,4,5-trichlorophenol	65.9	64.3

Table 2. Neutral compound distribution coefficients (K_d^0) determined from linear fits of K_d vs. chlorophenol ionization. With the exception of kappa number 4.93 data (r^2 = 0.90 and 0.60 for 2,4,5-TCP and 2,4-DCP, respectively) and cotton linter results (r^2 values of < 0.60), sorption data was strongly linear with r^2 values of > 0.97.

kappa number	2,4-DCP K_d^0(mL/g)	2,4,5-TCP K_d^0(mL/g)
0 (cellulose)	0.343	1.67
4.93	2.34	4.19
23.9	15.7	33.6
32.3	20.4	55.8
69.8	42.0	119
83.7	47.1	160
105	57.5	205
lignin precipitates	340	1200

Table 3. The effect of pulp fiber concentrations of the sorption of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers.

solids conc. (mg/L)	K_d(mL/g)
100	68.1
500	66.0
800	68.8
1250	65.5
2500	62.6
6250	60.8
12500	62.3

Figure Headings

Figure 1. Isotherm for the sorption of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers at 25^{0}C and pH 7.00.

Figure 2. Competitive isotherms for the sorption of 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers at 25^{0}C and pH 7.00.

Figure 3. Sorption of 2,4,5-trichlorophenol to kappa number 105 softwood fibers. The solid curve is a plot of equation 11.

Figure 4. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers.

Figure 5. Sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers as a function of the chlorophenol fraction in its neutral form.

Figure 6. Fiber-water distribution coefficients for 2,4-dichlorophenol and 2,4,5-trichlorophenol versus the kappa number of softwood fiber sorbents at pH 6.00.

Figure 7. Fiber-water distribution coefficients for 2,4-dichlorophenol and 2,4,5-trichlorophenol versus the kappa number of softwood fiber sorbents at pH 8.00.

Figure 8. Relationship between log K_1^0 and log K_{ow} values (data for toluene and trichloroethylene are from reference 16).

Figure 9. Temperature dependency plots for the sorption of 2,4-dichlorophenol and 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers at a pH of 4.00.

Figure 10. Sorption 2,4,5-trichlorophenol to kappa number 69.8 softwood fibers with no salt and 1 M KCl concentrations.

Figure 11. Sorption of 2,4-dichlorophenol to kappa number 105 softwood fibers as a function of the chlorophenol fraction in its neutral form with no salt and 1 M KCl concentrations.

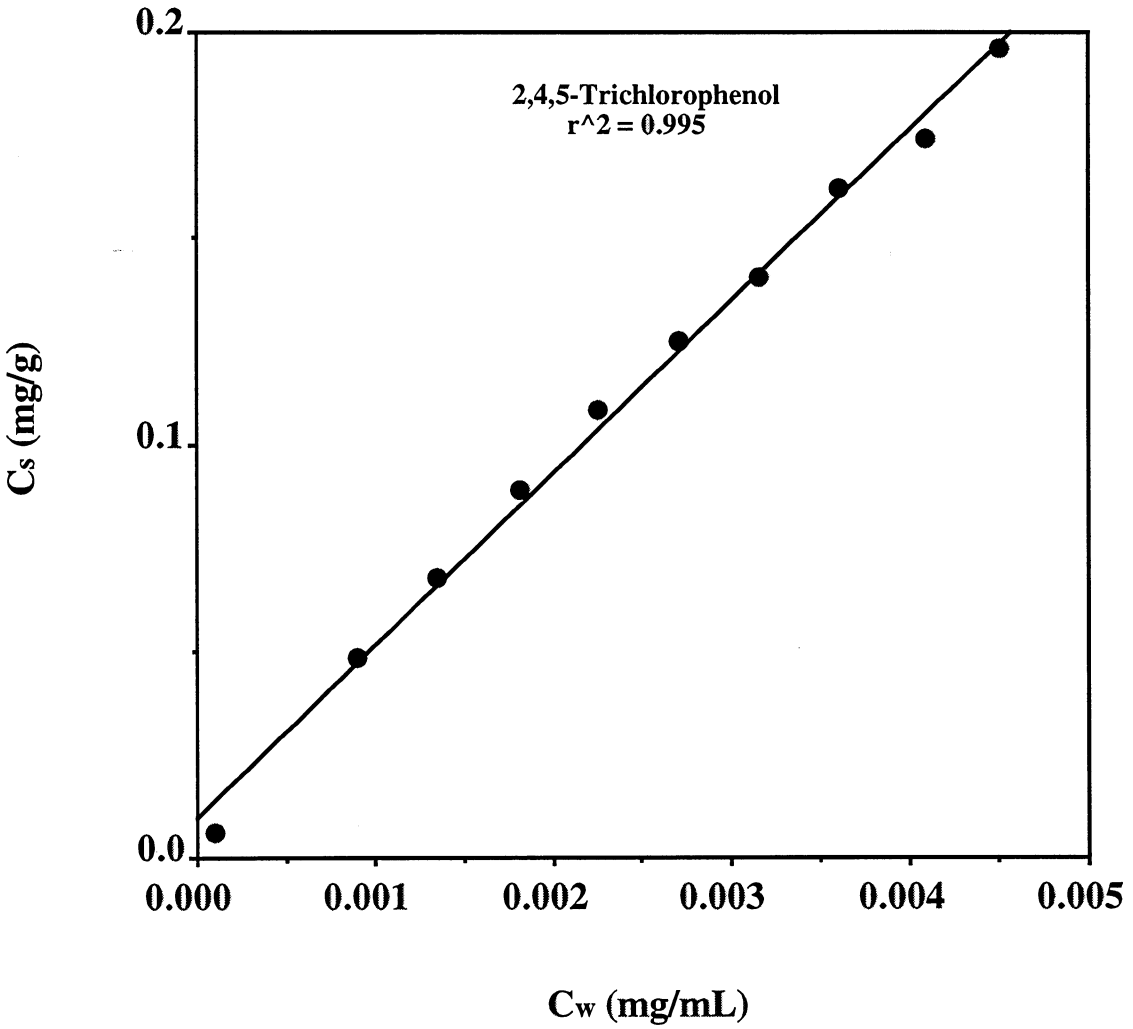
2,4,5-Trichlorophenol
r^2 = 0.995
0.2
0.1
0.0
0.000
0.001
0.002
0.003
0.004
0.005
Cs (mg/g)
Cw (mg/mL)

Fig. 1

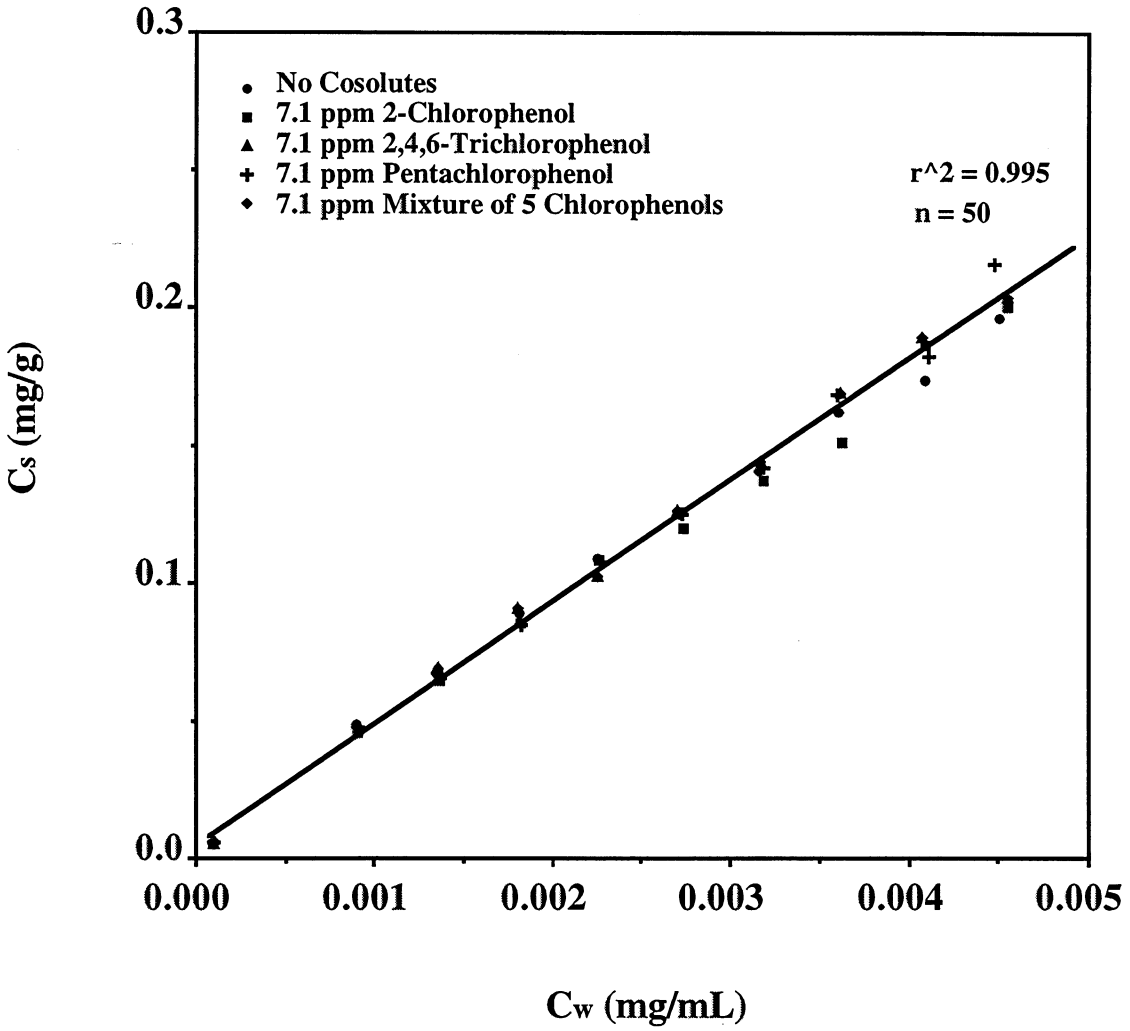
0.3
0.2
0.1
0.0
0.000
0.001
0.002
0.003
0.004
0.005
Cs (mg/g)
Cw (mg/mL)
No Cosolutes
7.1 ppm 2-Chlorophenol
7.1 ppm 2,4,6-Trichlorophenol
7.1 ppm Pentachlorophenol
7.1 ppm Mixture of 5 Chlorophenols
r^2 = 0.995
n = 50

Fig. 2

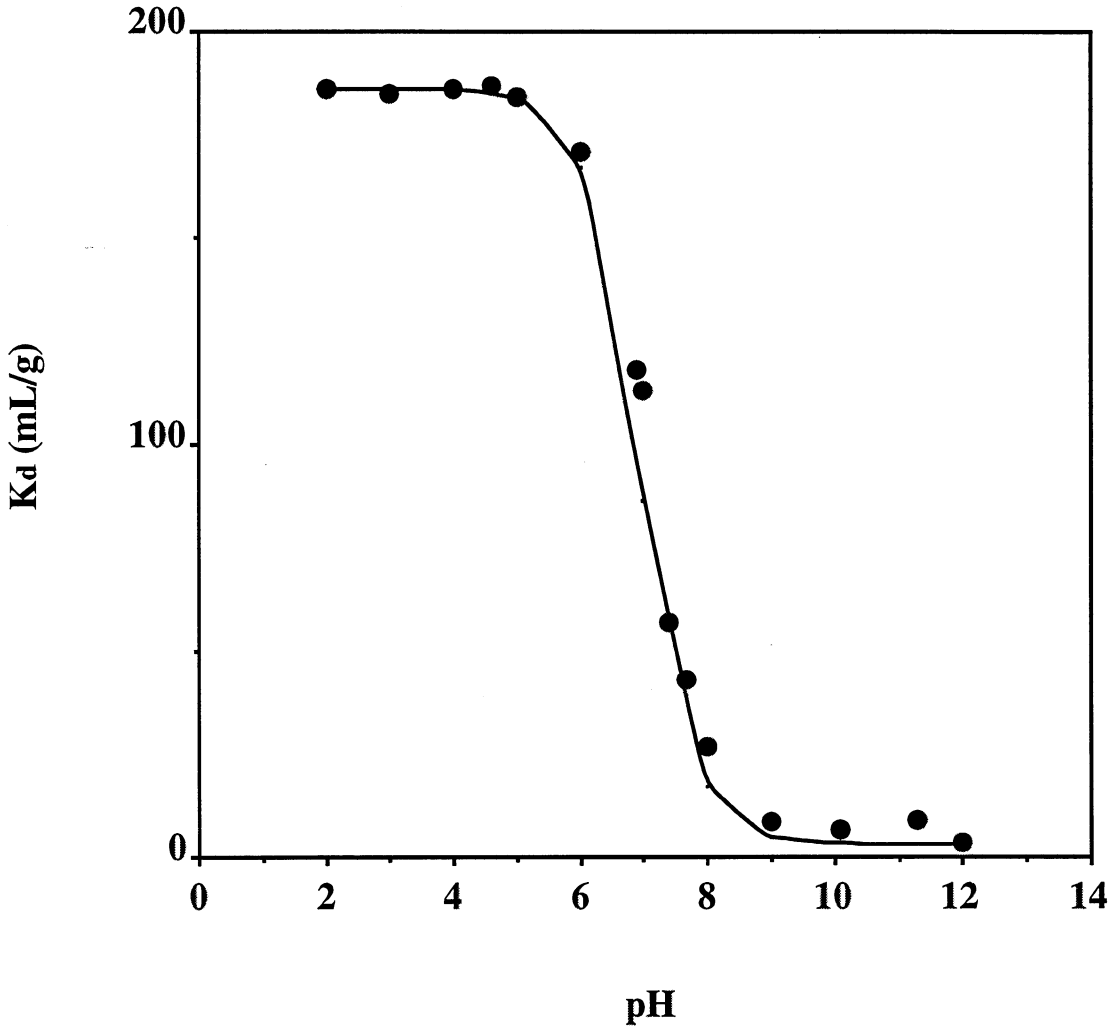

Fig. 3

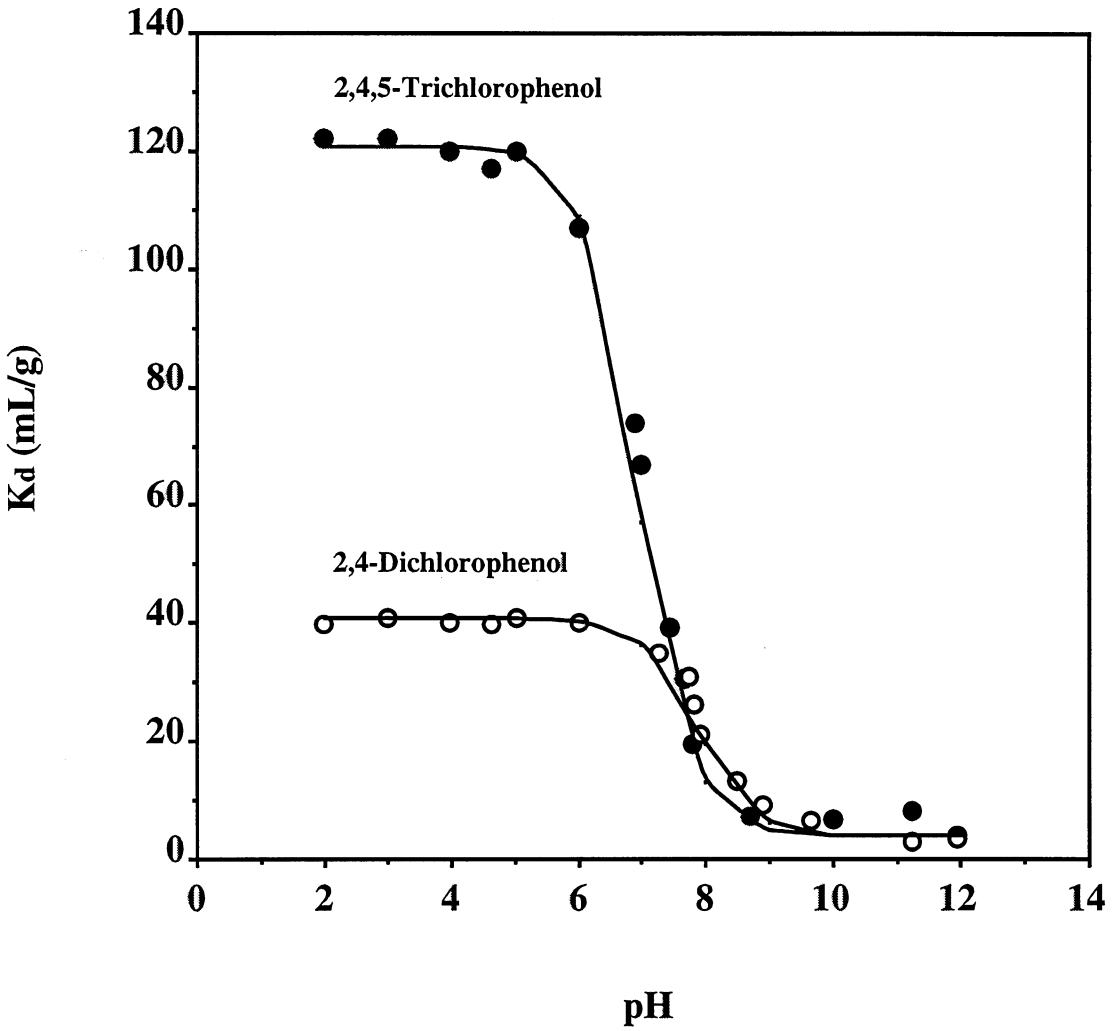
140
120
100
80
60
40
20
0
Kd (mL/g)
2,4,5-Trichlorophenol
2,4-Dichlorophenol
0
2
4
6
8
10
12
14
pH

Fig. 4

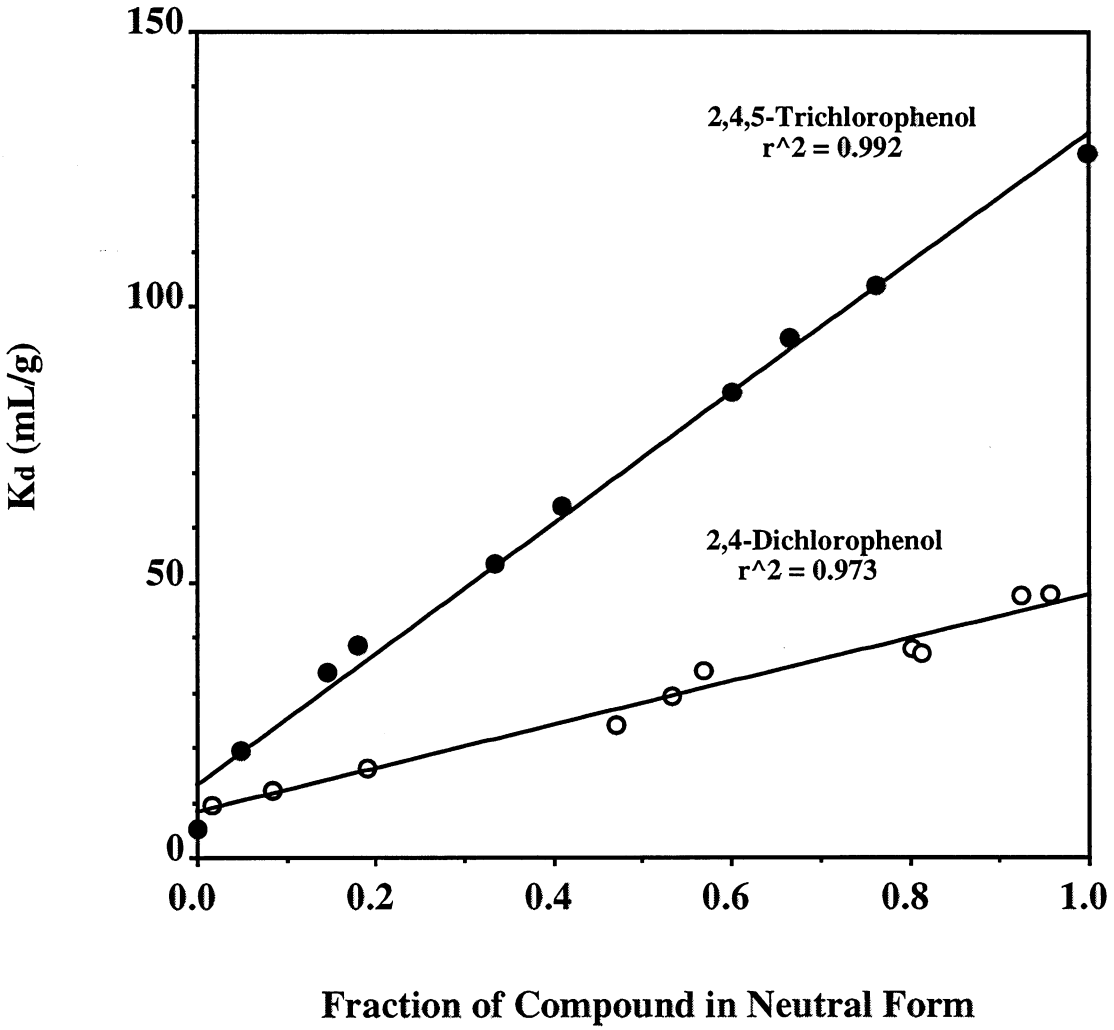
150
100
50
0
Kd (mL/g)
2,4,5-Trichlorophenol
r^2 = 0.992
2,4-Dichlorophenol
r^2 = 0.973
0.0
0.2
0.4
0.6
0.8
1.0
Fraction of Compound in Neutral Form

Fig. 5

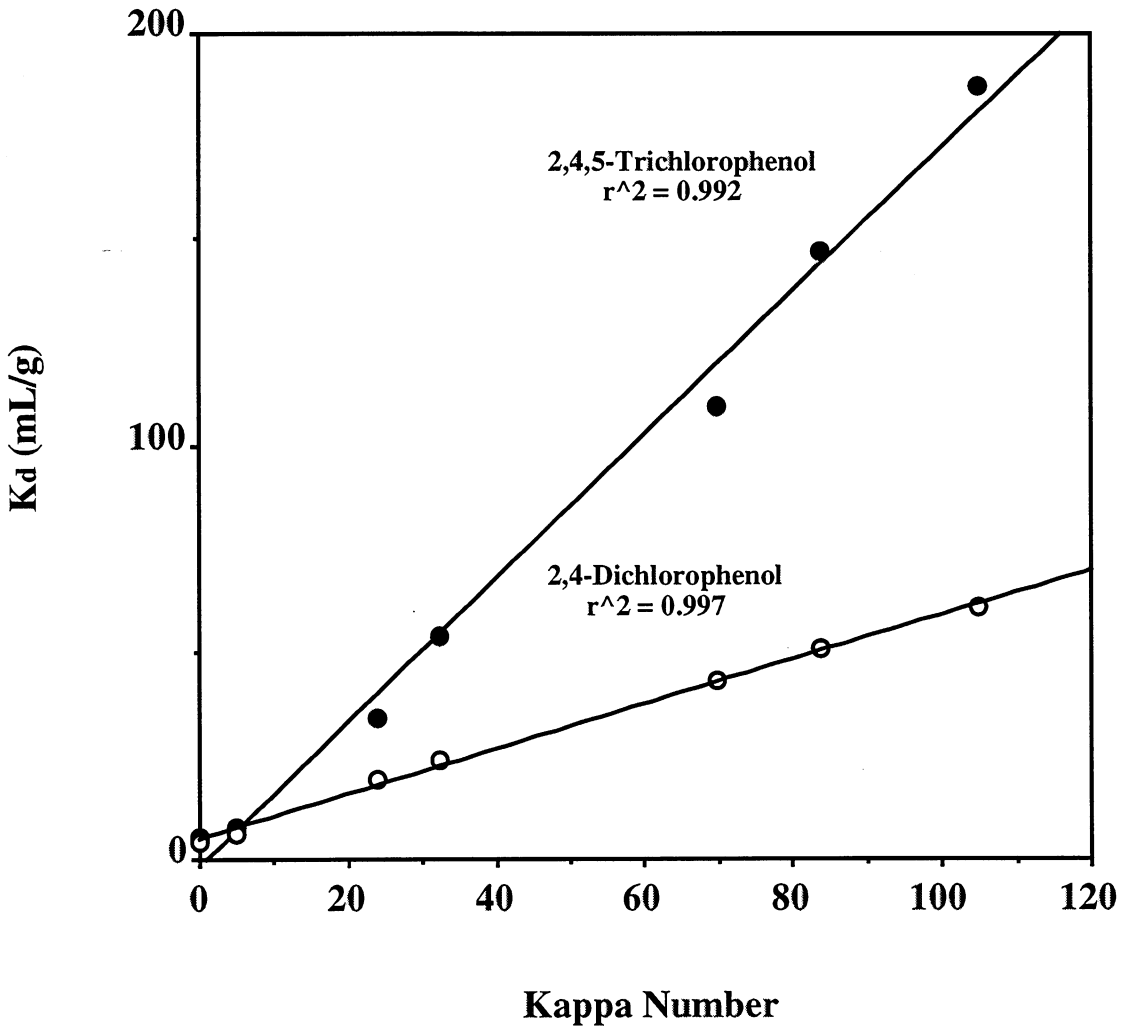
200
100
0
Kd (mL/g)
2,4,5-Trichlorophenol
r^2 = 0.992
2,4-Dichlorophenol
r^2 = 0.997
0
20
40
60
80
100
120
Kappa Number

Fig. 6

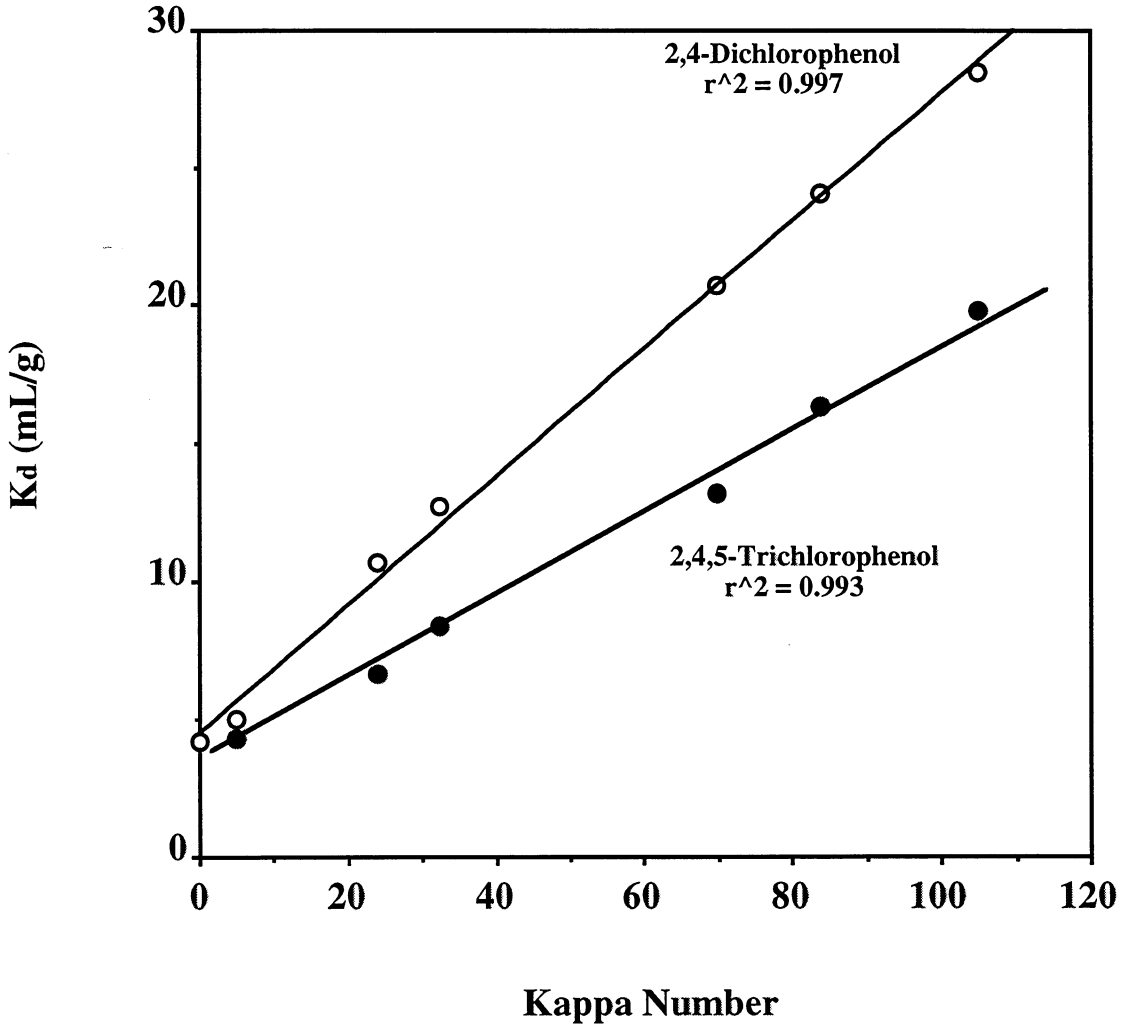
30
20
10
0
Kd (mL/g)
2,4-Dichlorophenol
r^2 = 0.997
2,4,5-Trichlorophenol
r^2 = 0.993
0
20
40
60
80
100
120
Kappa Number

Fig. 7

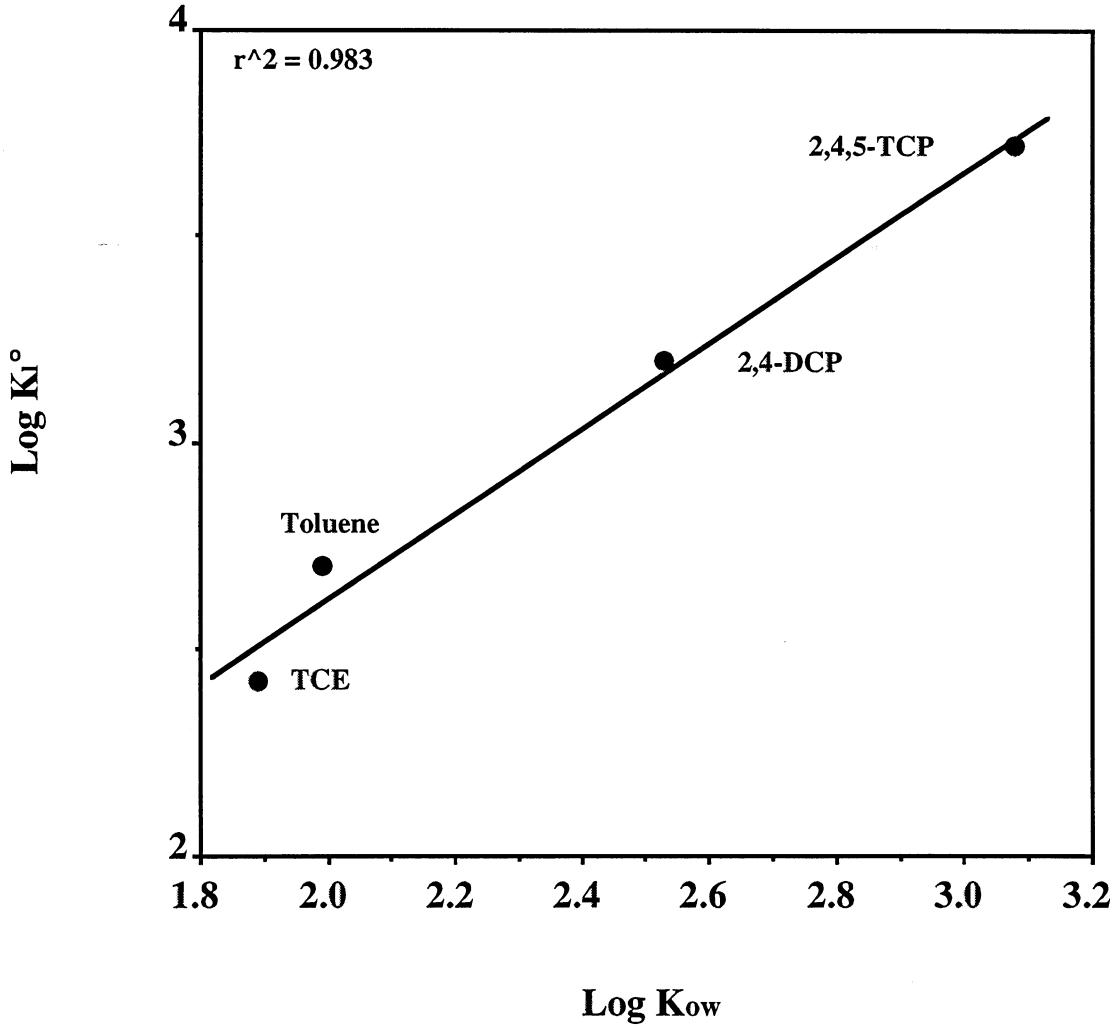
r^2 = 0.983
2,4,5-TCP
2,4-DCP
Toluene
TCE
4
3
2
1.8
2.0
2.2
2.4
2.6
2.8
3.0
3.2
Log Ki°
Log Kow

Fig. 8

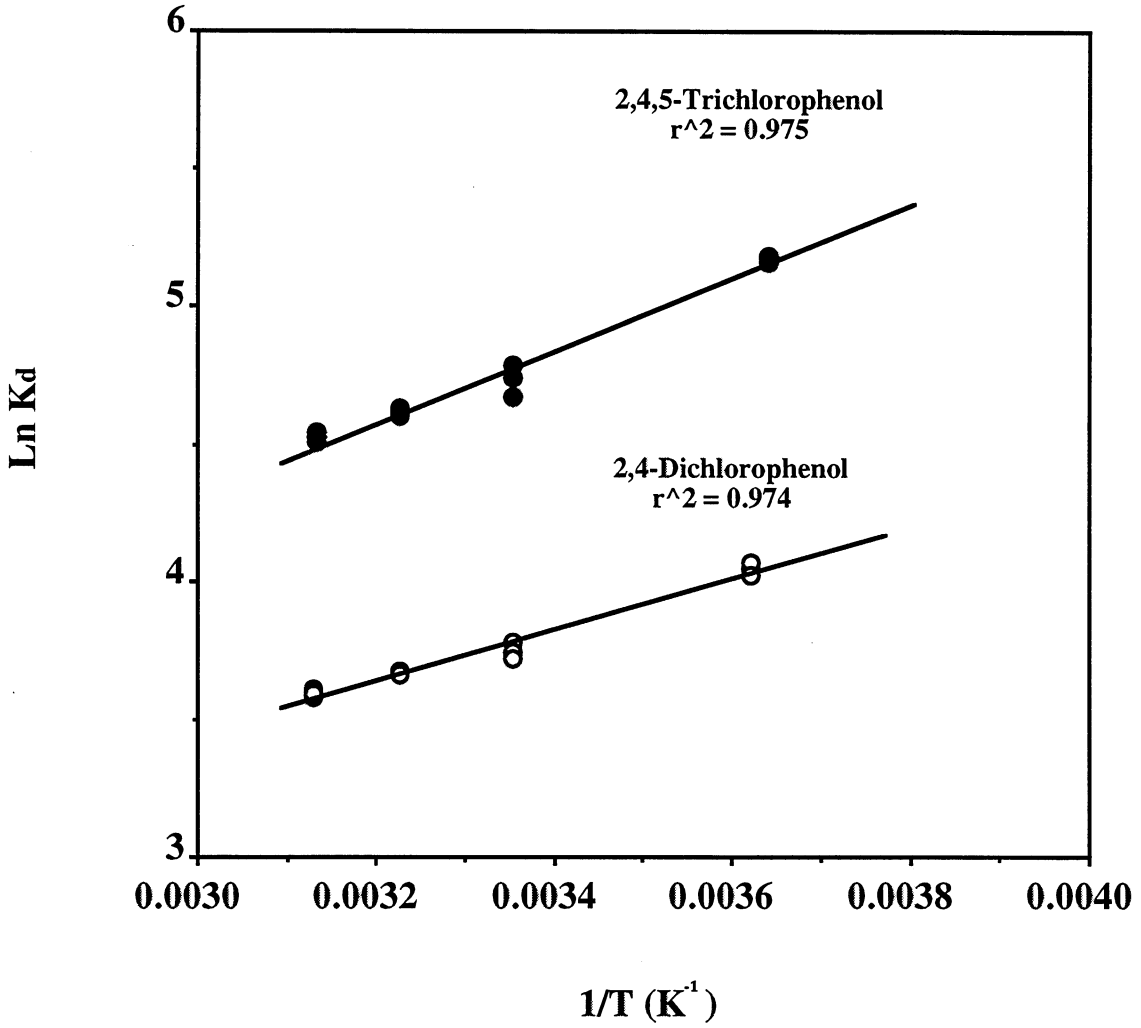
6
5
4
3
Ln Kd
2,4,5-Trichlorophenol
r^2 = 0.975
2,4-Dichlorophenol
r^2 = 0.974
0.0030
0.0032
0.0034
0.0036
0.0038
0.0040
1/T (K-1)

Fig. 9

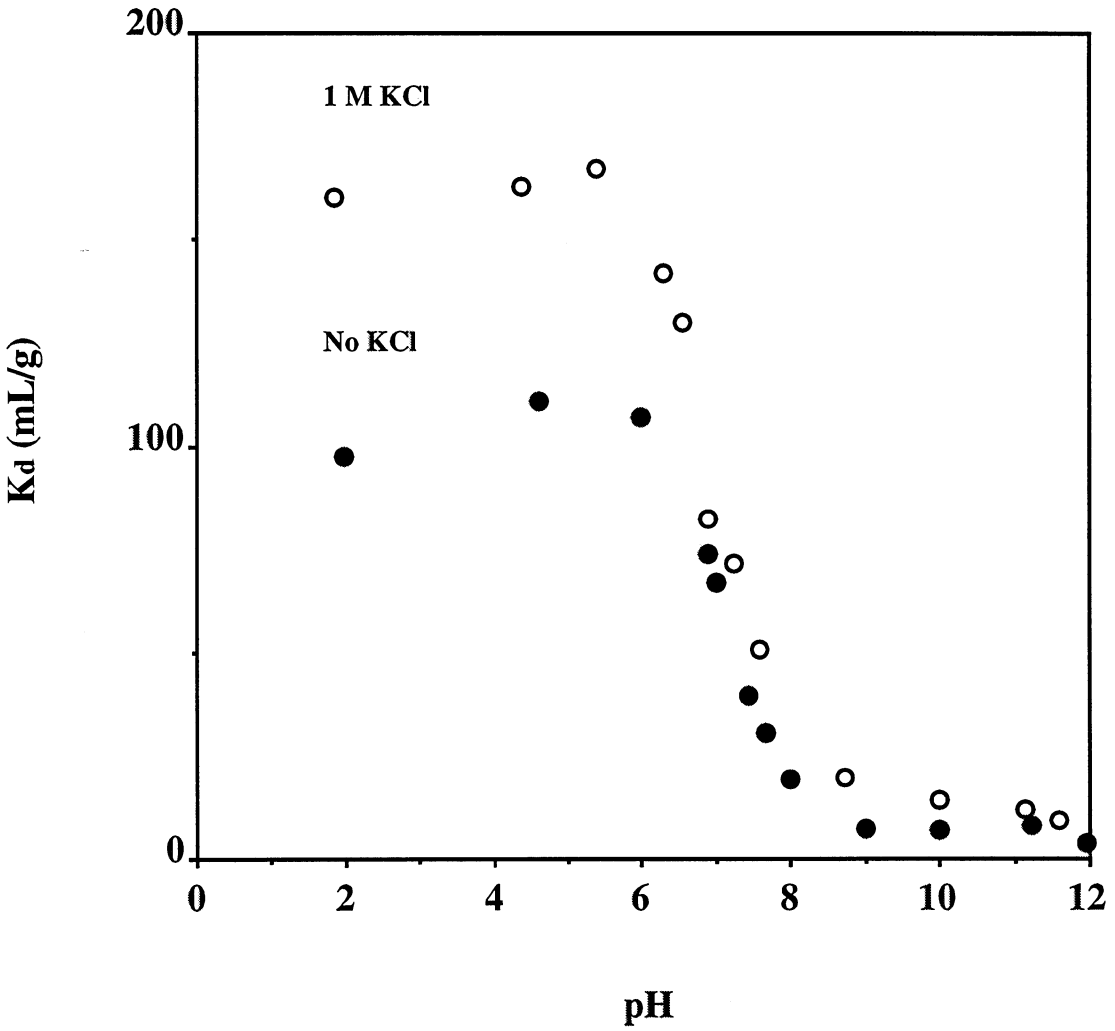

Fig. 10

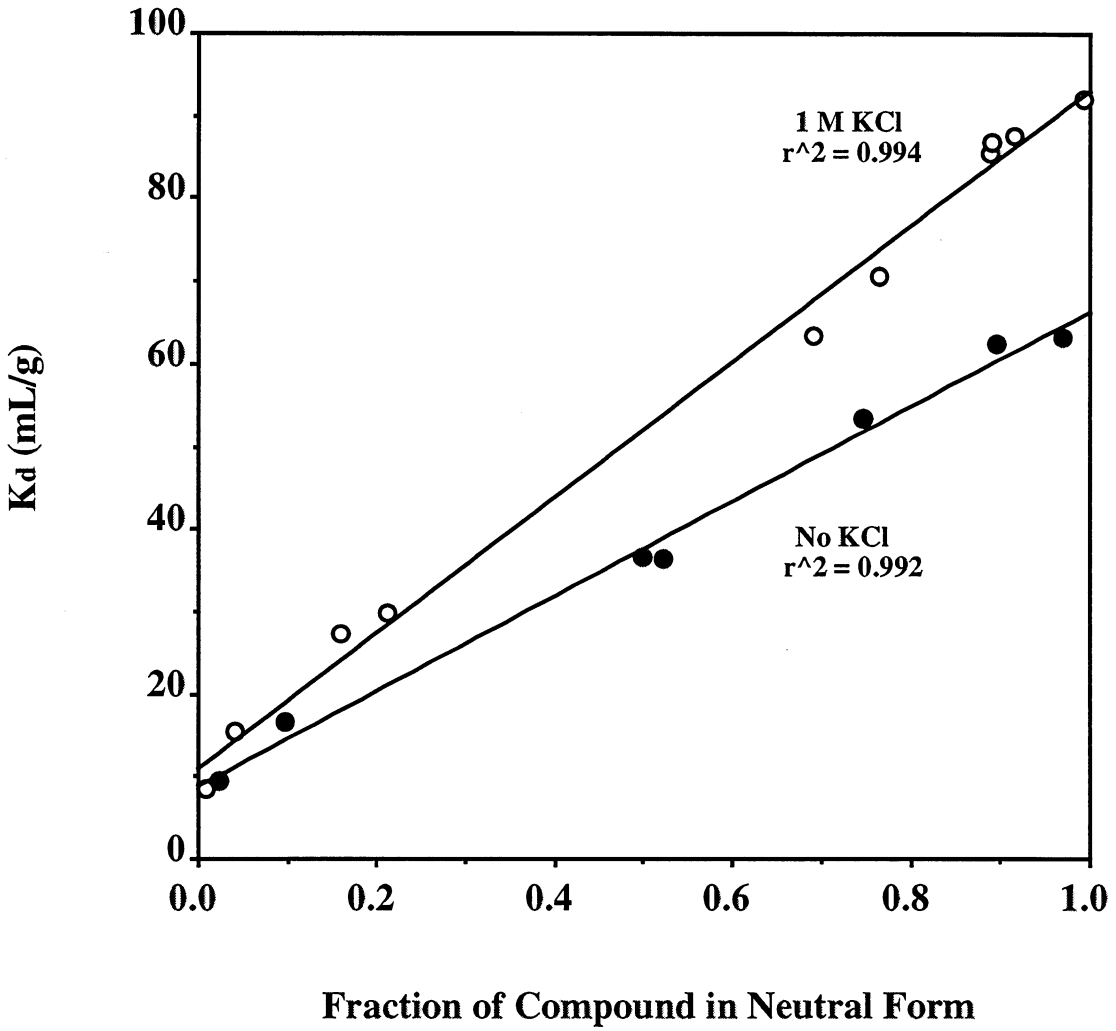
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
Kd (mL/g)
1 M KCl
r^2 = 0.994
No KCl
r^2 = 0.992
Fraction of Compound in Neutral Form

Fig. 11